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<p>(21) International Application Number: PCT/NO92/00096</p> <p>(22) International Filing Date: 22 May 1992 (22.05.92)</p> <p>(30) Priority data: 912006 24 May 1991 (24.05.91) NO</p> <p>(71) Applicant (for all designated States except US): SINVENT A/S [NO/NO]; N-7034 Trondheim (NO).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : EINARSRUD, Mari-Ann [NO/NO]; Saupstadringen 2E, N-7078 Saupstad (NO). HÆREID, Siv [NO/NO]; Balders vei 5A, N-7033 Trondheim (NO).</p> <p>(74) Agent: GØRBITZ, Johan, H.; Bryn & Aarflot A/S, Postboks 449 Sentrum, N-0104 Oslo (NO).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent), US.</p> <p>Published <i>With international search report.</i> <i>In English translation (filed in Norwegian).</i></p> <p>BEST AVAILABLE COPY</p>
<p>(54) Title: PROCESS FOR THE PREPARATION OF A SILICA AEROGEL-LIKE MATERIAL</p> <p>(57) Abstract</p> <p>A process for the preparation of silica xerogel by hydrolysis and polycondensation of a tetraalkoxysilane to form an alcogel which is a silica skeleton surrounded by an aqueous methanol, whereafter the aqueous methanol is removed by evaporation. The alcogel formed is brought in contact with a solution of tetraalkoxysilane, the contact is maintained at or above room temperature to strengthen the silica skeleton, whereafter the gel is dried slowly at or above room temperature and at about atmospheric pressure. Before the alcogel is brought in contact with the solution of tetraalkoxysilane it may be washed with a solution (e.g. aqueous methanol) to change the composition of the aqueous alcohol surrounding the silica skeleton or to change the functional groups on the surface of the alcogel.</p>		

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Process for the preparation of a silica aerogel-like material.

This invention relates to a process for the preparation of a material similar to silica aerogel. Silica aerogel is a porous material of a very low density and it contains up to 99% of air. The type of silica aerogel prepared according to the present invention is normally called silica xerogel. Due its high porosity, the material has excellent heat insulating properties, and since the pore size of the material is smaller than the wave length of visible light, it is also transparent. Typical properties of silica aerogel are as follows:

Density:	70 - 250 kg/m ³
Refractive index:	1.02 - 1.05
Thermal conductivity in air:	0.021 W/mK at 20°C
Thermal conductivity in vacuum:	0.008 W/mK at 20°C
Particle size:	4 - 7 nm
Pore size:	10 - 20 nm
Transmittance	88% for 10 mm thickness

Silica aerogel has an insulating property which is approximately twice as good as that of rockwool, and since it is also transparent, it may be used as insulation in windows. Due to its porosity silica xerogel/aerogel has also a very high capacity for sucking up liquid and may also be used as starting material for composite materials and carrier for catalyst and liquids, e.g. electrolytes.

Originally, sodium silicate-hydrate was used as starting material for the preparation of silica aerogel, and in a hydrogen chloride catalysed reaction between the silicate and water an aquagel was formed. However, this preparation route is very time-consuming since the aquagel has to be washed with alcohol before the drying step may take place. The drying process is necessary to remove preferably all liquid, leaving only the desired silica network.

More recently tetramethoxysilane, $\text{Si}(\text{OCH}_3)_4$, TMOS, has also been used as starting material for the preparation of silica aerogel. TMOS is a suitable starting material since it is easy to handle, easy to prepare in pure form and easy to hydrolyse. However, it is toxic and expensive. The alcogel formation takes place by a direct acid- and/or base-catalysed hydrolysis of TMOS in a so-called sol-gel technology. The alcogel formed is a silica skeleton surrounded by aqueous methanol. The problem which then arises is to remove the aqueous methanol from the silica skeleton to obtain the aerogel.

In order to prepare the desired aerogel, it is as mentioned above, necessary to remove the liquid surrounding the silica skeleton, and this may be done by eliminating or at least reducing the capillary forces working in the alcogel when the liquid front withdraws, or the network may be strengthened so that the pores do not collapse when the liquid is removed.

Two drying procedures are possible where the capillary forces are eliminated:

a) Supercritical drying where the solvent in liquid phase is transformed to the gaseous phase under elevated pressure in an autoclave at a temperature above the critical point of the solvent. A modification of this drying method is to extract the solvent with another compound such as CO_2 , which has lower critical point. Supercritical drying is a somewhat dangerous method because the large amounts of methanol which is expelled may lead to an explosion if there is a leak.

b) Freeze drying, where the alcogel is frozen to become solid, whereafter the solvent is subjected to sublimation under reduced pressure.

In the third possible method, viz.

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c) Air drying and direct evaporation of the solvent where the liquid phase is transformed to gaseous phase, the drying

process will normally lead to collapse of the pores and crack formation in the gel due to capillary forces. In the literature, the addition a DCCA (Drying Control Chemical Additive) to the sol has been reported, to obtain a narrow pore size distribution and hence a reduction in the differential strain in the alcogel, whereby cracking is considerably reduced. However, the resulting silica xerogel will have a relatively high density, e.g. about 1,4 g/cm³. Strictly speaking, only preparation method a) will result in an aerogel. In the other two methods b) and c) there will be obtained a gel which may be described as silica cryogel and silica xerogel respectively, which may have approximately the same properties as silica aerogel.

Drying method a) with supercritical drying results in an aerogel with low density and relatively good optical properties, but the method is expensive and dangerous due to the high pressure and the high temperature during drying. In the production of tiles for use as insulation in windows it will be necessary with an autoclave which will represent a considerable element of risk during operation due to large amounts of methanol which can be ignited. By using e.g. CO₂ as medium during the supercritical drying, an extraction of the solvent is necessary.

Drying method b) is cheap, but due to volume expansion of the solvent during crystallisation (i.e. freezing), the result may easily be cracking of the gel during the drying.

Drying method c) normally takes place with a large shrinkage of the gel due to a collapse of the gel structure. In the preparation of high density glass by sintering from these xerogels which are not particularly reactive, it is problematic to remove organic residues, i.e. DCCA.

The purpose of the present invention is to provide a process for preparing silica xerogel (aerogel) having a relatively low

density (i.e. below 0.5 g/cm^3) and such that the material is suitable as a heat insulating material.

According to present invention there is provided a new and improved process for the preparation of silica xerogel of low density by hydrolysis and polycondensation of a tetraalkoxysilane, to form a an alcogel which is a silica skeleton surrounded by aqueous alcohol. The process is characterised by the fact that the alcogel formed is contacted with a solution of a tetraalkoxysilane. The contact is maintained at or above room temperature to stabilise the silica skeleton, whereafter the alcogel is slowly dried at or above room temperature and at above approximately atmospheric pressure. Before the alcogel is contacted with the solution of tetraalkoxysilane it may be suitable to contact the alcogel with a liquid to wash the gel (in order to change the composition of the aqueous alcohol surrounding the silica skeleton) and to replace functional groups on the surface. This liquid may e.g. consist of a mixture of water and alcohol, preferably about 40% methanol. This liquid may also be replaced several times. The liquid added for washing may have a temperature up to the boiling point, preferably room temperature.

Suitably tetrametoxysilane is used for preparing the alcogel, whereafter the gel formed is contacted with a solution of tetraethoxysilane, e.g. in a lower alcohol, particularly methanol.

The contact between the alcogel and the later added tetraalkoxysilane is suitably maintained for a sufficiently long time for a strengthening of the gel network to take place, e.g. from 6 hours to 16 days, at a temperature which does not represent any risk for the alcogel, preferably from 20 to 200°C , particularly $40\text{--}80^\circ\text{C}$. An increased ageing time results in the largest pores in the product, i.e the lowest density. The washing of the alcogel with liquid, e.g aqueous

alcohol results in less shrinking of the gel and larger pores.

The alcohol used is normally a mono-, di- or trihydric alkanol, particularly with 1-10 C-atoms, preferably methanol.

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It is of essential importance that the drying takes place under controlled conditions, since a too quick drying may lead to collapse. Controlled drying may be accomplished by allowing it to take place in an atmosphere which contains components which are present in the liquid surrounding the silica skeleton, or components formed from said liquid at higher temperature. The drying may e.g. take place in a chamber with such an atmosphere, or it may take place while the alcogel is kept almost completely covered, e.g. up to 99%, whereby the same effect is obtained. The drying is suitably carried out at a temperature in the range 40 - 200°C. The drying temperature may also be gradually varied from room temperature to the boiling point of aqueous alcohol.

The thereby formed xerogel has a low density (e.g. 0,5 g/cm³ or lower) and has also a homogeneous structure.

Example 1

An alcogel was prepared by hydrolysis and polycondensation of TMOS. The hydrolysis took place with NH₄OH as catalyst, a stoichiometric amount of water (TMOS:water, molar ratio 1:4), and with methanol as a solvent. The gel formation took place at approximately 0°C. The alcogel was cast in Pyrex/teflon moulds with a removable bottom of Nescofilm. After up to several hours standing in completely covered condition after the gel formation, the mould with the alcogel was immersed in an ageing solution of tetraethoxysilane (TEOS) and methanol. The mould was removed from the bath after approximately 24 hours, and the bath was then kept covered for additional 24 hours. During the entire periode of immersing and continued storage, the temperature was kept at about 60°C. The gel was then covered to an extent of 97% and was dried at about 60°C

and a pressure of one atmosphere. The drying resulted in a monolithic gel having a density in the range 0.42 - 0.73 g/cm³. Different molar ratios between TEOS and methanol in the ageing solutions were used. The density decreases linearly, and correspondingly the pore size increases with increasing amount of TEOS in the ageing liquid and increased time in this liquid. The shrinkage of the alcogel during the drying is in the range 15 - 30% depending on the molar ratio and ageing time. The surface area of the xerogel is in the range 600 - 650 m²/g. The thermal conductivity of the silica xerogel material formed has been measured down to 0.024±0.004 W/mK at 45°C.

Example 2

An alcogel was prepared as described in Example 1. After up to several hours of standing in covered condition the moulded with the alcogel was immersed in liquid consisting of methanol and water (e.g. 30 volume % of water). The liquid mixture was changed three times with 24 hours intervals. The alcogel in the liquid mixtures was kept at room temperature during the entire washing. After four days the washing solution was replaced by a solution of tetraethoxysilane as in Example 1. The rest is as in Example 1.

The treatment of the alcogel in the solution of water and methanol causes less shrinkage of the alcogel during drying. The shrinkage of the alcogel during drying is about 13%. The thermal conductivity of the silica xerogel prepared has been measured down to 0.028±0.04W/mK.

The surface area decreases and the pore size increases linearly with increasing amount of water in the liquid mixture used for washing the alcogel.

Example 3

The same procedure as in Examples 1 and 2, but methanol was replaced by ethanol in the liquid mixture used during the

washing and as solvent for the tetraalkoxysilane used to strengthen the gel network.

C L A I M S

1. A process for the preparation of silica xerogel (aerogel) by hydrolysis and polycondensation of a tetraalkoxysilane to form an alcogel which is a silica skeleton surrounded by an aqueous alcohol, whereafter aqueous alcohol is removed by evaporation;
c h a r a c t e r i z e d i n t h a t the formed alcogel is brought in contact with a solution of tetraalkoxysilane, the contact is maintained at or above room temperature to strengthen the silica skeleton, whereafter the gel is dried slowly at or above room temperature at approximately atmospheric pressure.
2. The process of claim 1,
c h a r a c t e r i z e d i n t h a t the alcogel is brought in contact with a solution of tetraalkoxysilane, preferably in an alcohol.
3. The process of any of claims 1 and 2,
c h a r a c t e r i z e d i n t h a t the alcogel before further contact is washed with an optionally aqueous alcohol.
4. The process of any of claims 1 - 3,
c h a r a c t e r i z e d i n t h a t tetramethoxysilane is used for the preparation of the alcogel, which is then brought in contact with a solution of tetraethoxysilane in an alcohol, especially methanol.
5. The process of any of claims 1 - 4,
c h a r a c t e r i z e d i n t h a t the contact between the alcogel and the solution of tetraalkoxysilane is maintained at a temperature in the range 20 - 200°C for a period from 6 hours to 16 days.
6. The process of claim 5,
c h a r a c t e r i z e d i n t h a t the subsequent drying is performed within the temperature range 40 - 200°C.

7. The process of claim 6,
c h a r a c t e r i z e d i n t h a t the drying takes
place in an atmosphere which contains components present in
5 the liquid surrounding the silica skeleton, or components
which may be formed from the said liquid at higher
temperatures, for example by covering up to 99% of the gel
surface during drying.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/NO 92/00096**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 01/07/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
SE-B- 422045	82-02-15	AT-T- 1894	82-12-15
		EP-A-B- 0018955	80-11-12
		SE-A- 7903766	80-10-31
		US-A- 4327065	82-04-27
US-A- 4402927	83-09-06	NONE	
DE-A1- 3929219	90-03-29	NONE	
EP-A2- 0216278	87-04-01	AU-B- 588363	89-09-14
		AU-D- 6246986	87-03-26
		CA-A- 1280399	91-02-19
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		JP-A- 62072514	87-04-03
		US-A- 4775520	88-10-04
		US-A- 4911903	90-03-27

INTERNATIONAL SEARCH REPORT

International Application No PCT/NO 92/00096

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 01 B 33/157, 33/16																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black; padding: 2px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 2px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC5</td> <td style="padding: 5px;">C 01 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched⁸</div> <p style="padding: 5px;">SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 01 B											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; padding: 2px;">Category[*]</th> <th style="width: 60%; border-bottom: 1px solid black; padding: 2px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%; border-bottom: 1px solid black; padding: 2px;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">SE, B, 422045 (G. VON DARDEL ET AL) 15 February 1982, see the whole document —</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4402927 (GUY VON DARDEL ET AL) 6 September 1983, see the whole document —</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">DE, A1, 3929219 (VEB LEUNA-WERKE) 29 March 1990, see the whole document —</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0216278 (MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG) 1 April 1987, see the whole document — —————</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	SE, B, 422045 (G. VON DARDEL ET AL) 15 February 1982, see the whole document —	1-7	A	US, A, 4402927 (GUY VON DARDEL ET AL) 6 September 1983, see the whole document —	1-7	A	DE, A1, 3929219 (VEB LEUNA-WERKE) 29 March 1990, see the whole document —	1-7	A	EP, A2, 0216278 (MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG) 1 April 1987, see the whole document — —————	1-7
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>^{"X"} document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"Y"} document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>^{"a"} document member of the same patent family</p> </div> </div>																	
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